

UC Irvine

UC Irvine Previously Published Works

Title

Effects of Pb Content on the Formation of the High-TcPhase in the (Bi, Pb)-Sr-Ca-Cu-O System

Permalink

<https://escholarship.org/uc/item/8ht342q1>

Journal

Japanese Journal of Applied Physics, 28(2)

ISSN

0021-4922

Authors

Rhee, CK
Kim, CJ
Lee, HG
[et al.](#)

Publication Date

1989-07-20

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Effects of Pb Content on the Formation of the High- T_c Phase in the (Bi, Pb)-Sr-Ca-Cu-O System

C. K. RHEE, C. J. KIM, H. G. LEE, I. H. KUK,
J. M. LEE, I. S. CHANG, C. S. RIM, P. S. HAN,
S. I. PYUN[†] and D. Y. WON

Korea Advanced Energy Research Institute, P.O. Box 7, Daedok Science Town, Daejeon, 302-353, Korea

[†]Department of Materials Science, Korea Advanced Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul, Korea

(Received March 18, 1989; accepted for publication June 12, 1989)

Formation of the high- T_c phase in the (Bi, Pb)-Sr-Ca-Cu-O system was studied using specimens with various Bi/Pb ratios. The synthesis temperature was suppressed as the Pb/(Pb+Bi) was increased. The lattice constant of the c axis of the low- T_c phase ($T_c \sim 80$ K) and high- T_c phase ($T_c \sim 105$ K) increased with increasing Pb content. Substitution of 30% Pb for Bi was found to be most preferential for the formation of the high- T_c phase.

KEYWORDS: (Bi+Pb)-Sr-Ca-Cu-O superconductor, Pb content, high- T_c phase, lattice parameter

Since the discovery of the high- T_c phase in the BiSrCaCuO system,¹⁾ many studies dealing with element substitution have been made in attempts to separate the high- T_c phase ($T_c \sim 105$ K) from the low- T_c phase ($T_c \sim 80$ K).

Recently, Takano *et al.*²⁾ reported that the substitution of Pb for Bi in the BiSrCaCuO system promoted and enhanced the formation of the high- T_c phase ($T_c = 107$ K). Very recently, the effects of oxygen partial pressure on the formation of the high- T_c phase,³⁾ the modulation structure,⁴⁾ the possible role of PbO as a flux to form the high- T_c phase,⁵⁾ and the occupation of Pb on Bi sites were reported in the Pb-doped BiSrCaCuO system.⁶⁾ However, the role of Pb in the BiSrCaCuO system is still unclear.

The purpose of this work was to investigate the effects of Pb addition on the formation of the high- T_c phase in the BiSrCaCuO system by changing the amount of Pb added.

$\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_{1.8}\text{O}_y$ samples ($x=0.1, 0.2, 0.3,$ and 0.4) were prepared by the solid-state reaction of Bi_2O_3 , PbO , SrCO_3 , CaO , and CuO powders. Powder mixtures were well mixed, calcined at 800°C for 20 h and then well crushed. Pressed pellets were sintered at 845°C , 855°C , and 865°C for various periods. All the heat treatments were performed in air and, air quenching was carried out after sintering. The structure of the samples was examined by X-ray diffraction (XRD) and their electrical resistances were measured by the ac four probe method. Differential thermal analysis was also carried out with calcined powders in order to determine where melting occurs.

Superconducting-to-normal transition temperature (T_c , $R=0$ point) of $\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_{1.8}\text{O}_y$ is shown as a function of sintering time in Fig. 1. Sintering was performed at 855°C in air. Samples with $x \leq 0.3$ show zero resistivity above 77 K after sintering for 96 h and then a T_c of ~ 100 K is achieved by further heat treatment for 240 h. However, for the sample with $x=0.4$, zero resistivity above 77 K appears after a long-term annealing period of

220 h where the T_c is 95 K. Moreover, there exists an extra resistance drop at ~ 105 K. From the above results, it can be said that the formation of the high- T_c phase is clearly delayed when the amount of Pb addition is excessive. Recently, Uzumaki *et al.*⁷⁾ reported that the formation of the high- T_c phase underwent liquid phase sintering. In general, the grain growth rate may be delayed if the liquid phase existing at the grain boundaries is increased. Therefore, it is considered that the delay of the formation of the high- T_c phase for the specimen with $x=0.4$ is due to the presence of a large amount of a liquid phase.

Figure 2 shows the variation of T_c as a function of sintering time for the samples with $x=0.1$ and 0.2 which were sintered at 865°C . It can be seen that zero resistivity above 77 K appears after sintering for ~ 30 h. However, for $x=0.3$ and 0.4 , the samples were partially melted at this temperature and reacted with an alumina substrate. Therefore, they did not show zero resistivity down to 77 K. DTA (differential thermal analysis) data of calcined powders indicated that the melting point of the sample

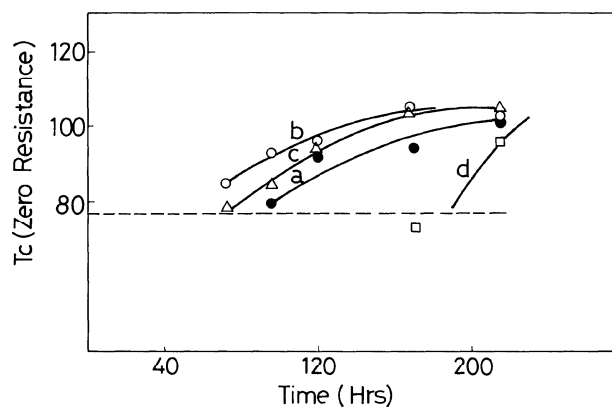


Fig. 1. T_c ($R=0$ point) vs sintering time for the specimens of $\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_{1.8}\text{O}_y$. Sintering was performed at 855°C and Pb content x was (a) 0.1, (b) 0.2, (c) 0.3 and (d) 0.4.

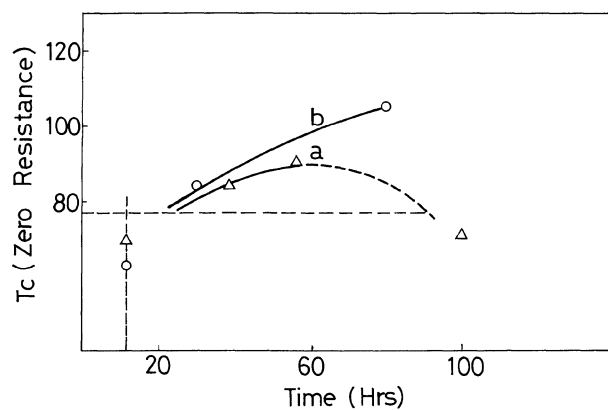


Fig. 2. T_c ($R=0$ point) vs sintering time for the specimens of $\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_{1.8}\text{O}_y$. Sintering was performed at 865°C and Pb content x was (a) 0.1 and (b) 0.2.

decreased as the amount of Pb was increased; e.g., 871°C for $x=0.1$ and 865°C for $x=0.3$. The endothermic peak at lower temperatures ($\sim 840^\circ\text{C}$)⁸ was not detected. It was also observed that the formation of the liquid phase resulted in the suppression of the formation of the high- T_c phase and the enhancement of the formation of the $\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_5\text{O}_y$ bronze-colored phase. It was very noticeable that the T_c was decreased by extended heat treatment for ≥ 60 h. From the observations of Figs. 1 and 2, it is seen that T_c was increased with increasing sintering time when the sintering temperature was 855°C . In contrast, the T_c has a maximum of 95 K after sintering for 50 h and then decreases after further annealing when the heat treatment temperature is as high as 865°C .

XRD data of the samples are shown in Fig. 3. The amount of Pb content was 0.3 and sintering was performed at 855°C for 220 h in air. As previously reported,⁹ it can be seen that the diffraction peaks from the low- T_c and high- T_c phases appear as a mixed state. It can also be recognized that an XRD peak of PbCa_2O_4 appears at $2\theta=17.48^\circ$. The intensity of the XRD peak of PbCa_2O_4 was strengthened as the amount of Pb was increased.

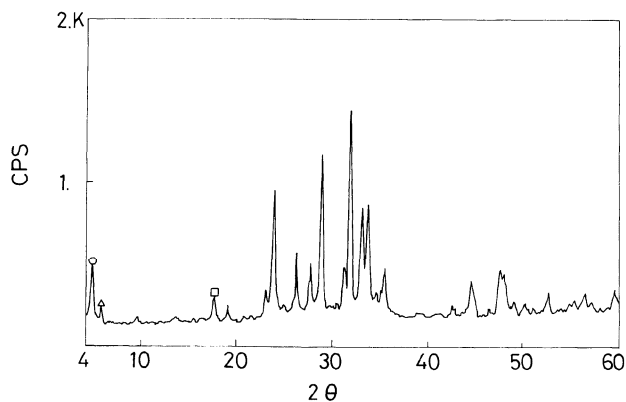


Fig. 3. XRD pattern for the specimen with $x=0.3$. Sintering was performed for 220 h at 855°C . Δ and \circ indicate the (002) peaks of low- T_c and high- T_c phases, respectively. \square indicates the XRD peak of PbCa_2O_4 .

In general, the volume fraction of a phase in a multiphase system is dependent on the integrated peak intensity if the sample has no preferred orientation. In Fig. 4, $I(0012)_h/I(0012)_l$ is represented as a function of the Pb content. It can be seen that $I(0012)_h/I(0012)_l$ increases as the Pb content is increased up to 0.3 and then slightly decreases for $x=0.4$. In Fig. 5, the variation of the c

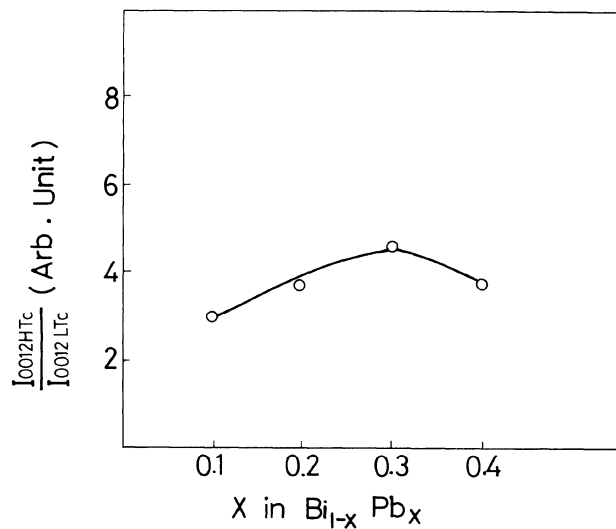


Fig. 4. Variation of $I(0012)_h/I(0012)_l$ as a function of Pb content x . $I(0012)_h$ and $I(0012)_l$ indicate the (0012) peak of high- T_c and low- T_c phases, respectively.

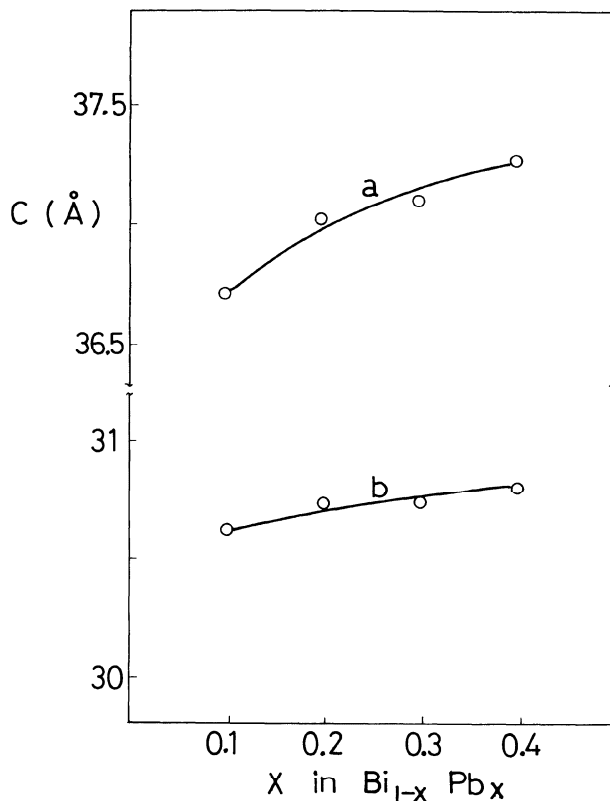


Fig. 5. Variation of the c parameter of the unit cell as a function of the Pb content x . (a) c parameter of the high- T_c phase and (b) c parameter of the low- T_c phase.

parameter of the unit cell is shown as a function of the Pb content. It can be seen that the c axes of the high- T_c and low- T_c phases are increased as the Pb content is increased. Ono¹⁰⁾ reported the increase of the c parameter when the Ca/Sr ratio is decreased in the BiSrCaCuO system. Very recently, Nobumasa *et al.*,¹¹⁾ using high-resolution analytical electron microscopy (HRAEM), directly observed that the Pb atoms were located in the Bi-O layers with an atomic ratio of Pb/Bi \sim 0.1. From the results, it is considered that Pb atoms were substituted into the Bi sites in the BiSrCaCuO system which led to the increase of the c axes of the high- T_c phases as well as the low- T_c phase. Additionally, the monotonic increase of the c axes with Pb content infers that the Pb/Bi ratio increases as the amount of Pb is increased in the Pb-doped BiSrCaCuO system.

In summary, samples of $\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_{1.8}\text{O}_y$ were prepared and the structure and the superconducting properties of the samples were investigated. It was observed that the Pb addition of 30% is the most preferable for the formation of the high- T_c phase in a $\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_{1.8}\text{O}_y$ system. The formation of the high- T_c phase was delayed by the excessive addition of Pb(40%). It was also observed that the lattice parameter, c , of the unit cell of the low- T_c and high- T_c phases was increased with increasing the Pb content.

Acknowledgements

This work was supported by the Ministry of Science and Technology, Korea. The Authors would like to thank Messrs. Ki-B. Kim, Kyung-S. Lim and Man. K. Chung for their help through the experiment.

References

- 1) H. Maeda, T. Tanaka, M. Fukutomi and T. Asano: Jpn. J. Appl. Phys. **27** (1988) L209.
- 2) M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tomii and H. Mazaki: Jpn. J. Appl. Phys. **27** (1988) L1041.
- 3) U. Endo, S. Koyama and T. Kawai: Jpn. J. Appl. Phys. **27** (1988) L1476.
- 4) S. Ikeda, K. Aota, T. Hatano and K. Ogawa: Jpn. J. Appl. Phys. **27** (1988) L2040.
- 5) N. Kijima, H. Endo, J. Tsuchiya, A. Sumiyama, M. Mizuno and Y. Oguri: Jpn. J. Appl. Phys. **27** (1988) L1852.
- 6) U. Endo, S. Koyama and T. Kawai: Jpn. J. Appl. Phys. **28** (1989) L190.
- 7) T. Uzumaki, K. Yamanaka, N. Kamehara and K. Niwa: Jpn. J. Appl. Phys. **28** (1989) L75.
- 8) T. Hatano, K. Aota, S. Ikeda, K. Nakamura and K. Ogawa: Jpn. J. Appl. Phys. **27** (1988) L2055.
- 9) H. G. Lee, C. J. Kim, K. H. Lee and D. Y. Won: Appl. Phys. Lett. **54** (1989) 391.
- 10) A. Ono: Jpn. J. Appl. Phys. **27** (1988) L2276.
- 11) H. Nobumasa, T. Arima, K. Shimizu, Y. Otsuka, Y. Murata and T. Kawai: Jpn. J. Appl. Phys. **28** (1989) L57.